

# Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US05/009441

International filing date: 21 March 2005 (21.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: US  
Number: 60/555,281  
Filing date: 22 March 2004 (22.03.2004)

Date of receipt at the International Bureau: 25 April 2005 (25.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland  
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

1308906

# THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

*April 15, 2005*

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.**

**APPLICATION NUMBER: 60/555,281**

**FILING DATE: *March 22, 2004***

**RELATED PCT APPLICATION NUMBER: *PCT/US05/09441***



Certified by

Under Secretary of Commerce  
for Intellectual Property  
and Director of the United States  
Patent and Trademark Office

20427 U.S. PTO  
032204

PTO/SB/16 (01-04)  
Approved for use through 07/31/2006. OMB 0651-0032  
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE  
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EJ52569836US

22151 U.S. PTO  
60/555281

032204

INVENTOR(S)					
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)	
George Albert		Farthing, Jr.		Alliance, Oh	
Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GASES					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input checked="" type="checkbox"/> Customer Number: 000041669					
OR					
<input type="checkbox"/> Firm or Individual Name					
Address					
Address					
City		State		Zip	
Country		Telephone		Fax	
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification Number of Pages 4		<input type="checkbox"/> CD(s), Number _____			
<input checked="" type="checkbox"/> Drawing(s) Number of Sheets 3		<input checked="" type="checkbox"/> Other (specify) Return Postcard			
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE Amount (\$)	
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees.				160.00	
<input checked="" type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 50-1831					
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.					
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

[Page 1 of 2]

Respectfully submitted,

SIGNATURE

TYPED or PRINTED NAME Michael J Seymour

TELEPHONE (330) 860-6605

Date March, 22, 2004

REGISTRATION NO. 54,436

(if appropriate)

Docket Number: Case 7102

**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

**PROVISIONAL APPLICATION COVER SHEET**  
**Additional Page**

PTO/SB/16 (08-03)

Approved for use through 07/31/2006. OMB 0651-0032

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Docket Number Case 7102

INVENTOR(S)/APPLICANT(S)		
Given Name (first and middle [if any] )	Family or Surname	Residence (City and either State or Foreign Country)
William	Downs	Alliance, Ohio

[Page 2 of 2]

Number 1 of 1

**WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

## **DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GAS**

### **[001] BACKGROUND OF INVENTION**

[002] Emissions Standards, as articulated by the U.S. Environmental Protection Agency (EPA), require assessment of hazardous air pollutants from utility power plants. Coal-fired utility boilers are a known source of anthropogenic mercury emissions in the United States. The EPA recently articulated the need to regulate mercury emissions from coal- and oil-fired utility units.

Accordingly as elemental mercury and many of its compounds are volatile, conventional electric utility plant air pollution control methods fail to meet advancing EPA standard requiring new methods and processes to be developed.

[003] Mercury appears in coal combustion flue gases in both the solid and gas phases, particulate-bound mercury and vapor-phase mercury, respectively. Due to the high volatility of mercury and many of its compounds, most of the mercury found in flue gases is vapor-phase mercury. Vapor-phase mercury, can appear as elemental mercury (elemental, metallic mercury vapor) or as oxidized mercury (vapor-phase species of various compounds of mercury). Speciation, the form of mercury present, is a key factor in the development of mercury emissions control strategies.

[004] Particulate collectors in use at electric utility plants, most commonly electrostatic precipitators (ESP) or fabric filters (FF), sometimes called baghouses, provide high-efficiency removal of particulate-bound mercury. Fabric filters tend to exhibit better mercury removal than ESP's by providing more intimate contact between the flue gases and fly ash as the flue gases pass through the filter cake of fly ash on the filter bags. This intimate contact may promote the

Date Filed: Filed March 22, 2004

**Title: DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GAS**

adsorption of vapor-phase mercury species onto the fly ash or unburned carbon particles in the filter cake. Both wet and spray dryer absorber (SDA) flue gas desulfurization (FGD) systems remove significant amounts of oxidized mercury. Oxidized mercury, typically appearing in the form of mercuric chloride, is soluble in water, making it amenable to removal in sulfur dioxide scrubbers. Elemental mercury, insoluble in water, passes through most scrubbers. Removal of elemental mercury, therefore, remains an important issue in the search for cost-effective mercury control techniques.

[005] Numerous studies have been, and continue to be, conducted to develop cost-effective approaches to the control of elemental mercury. Many of the studies have focused on the injection of a carbonaceous sorbent (e.g., powdered activated carbon, or PAC) into the flue gas stream to adsorb vapor-phase mercury. The sorbent, and its burden of adsorbed mercury, are subsequently removed from the flue gases in a downstream particulate collector. Adsorption is a technique that has often been successfully applied for the separation and removal of trace quantities of undesirable components. PAC injection is used, commercially, to remove mercury from municipal waste combustor exhaust gases. PAC injection removes both oxidized and elemental mercury species, although removal efficiencies are higher for the oxidized form. Although this approach appeared attractive in early work, the economics of high injection rates can be prohibitive when applied to coal-fired utility plants. More refined studies are now in progress to define more precisely what can and cannot be achieved with PAC. Still other studies seek to enhance PAC technology. One technique subjects the PAC to an impregnation process wherein elements such as iodine or sulfur are incorporated into the carbonaceous sorbent. Such processes can yield sorbents that more strongly bond with adsorbed mercury species, but also result in significantly higher sorbent cost.

Date Filed: Filed March 22, 2004

**Title: DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GAS**

[006] The speciation of vapor-phase mercury depends on coal type. Eastern U.S. bituminous coals tend to produce a higher percentage of oxidized mercury than do western subbituminous and lignite coals. Western coals have low chloride content compared to typical eastern bituminous coals. It has been recognized for several years that a loose empirical relationship holds between the chloride content of coal and the extent to which mercury appears in the oxidized form. Figure 1 illustrates the relationship between coal chlorine content and vapor-phase mercury speciation. An important reason for the significant uncertainty (scatter) in the data of Figure 1 is that mercury oxidation proceeds by both homogeneous and heterogeneous reaction mechanisms. Boiler convection pass and combustion air preheater temperature profiles, flue gas composition, fly ash characteristics and composition, and the presence of unburned carbon have all been shown to affect the conversion of elemental mercury to oxidized mercury species.

[007] It has been determined that the reactivity of conventional PAC (PAC that has not undergone special treatment such as iodine impregnation) with elemental mercury vapor is dependent upon the presence of acid gas species (e.g., hydrogen chloride and sulfur trioxide) in the flue gas stream. The presence of hydrogen chloride (HCl), in particular, has been shown to significantly improve the adsorption of elemental mercury from coal combustion flue gases. The hydrogen chloride is apparently adsorbed onto the carbon surface, facilitating the subsequent adsorption of elemental mercury. It is believed that an oxidized form of mercury is formed on the carbon surface. This phenomenon is of great practical importance for the application of PAC injection for mercury control for plants firing subbituminous and lignite coals. These coals tend to have very low chlorine content, and therefore produce combustion gases containing only small amounts of hydrogen chloride, and therefore would benefit significantly by the addition of hydrogen chloride in judicious ways.

Date Filed: Filed March 22, 2004

Title: DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GAS

[008] The dearth of halogen-containing gases can be further exacerbated if the PAC injection process is operating downstream of a sulfur dioxide scrubber, such as a wet or SDA FGD system. The scrubber removes acid gases such as hydrogen chloride in addition to the removal of sulfur dioxide. As an example, consider the application of PAC injection to a unit equipped with SDA FGD and a fabric filter that fires a low-chlorine coal. The concentration of hydrogen chloride in the flue gases resulting from the combustion of these coals is low. This concentration is further reduced by absorption in the SDA FGD system. This renders the PAC largely ineffective for elemental mercury capture in the SDA FGD and fabric filter. PAC must therefore be injected sufficiently far upstream of the SDA FGD to allow for the capture of mercury prior to the removal of the acid gases in the SDA FGD. This significantly limits the effective residence time available for mercury removal, and necessitates the use of high carbon injection rates. In addition to cost, high quantities of carbon can also limit ash disposal and/or utilization options.

[009] Felsvang, et. al. (U.S. Patent 5,435,980) teaches that the mercury removal of a coal-fired system employing an SDA FGD system can be enhanced by increasing the chlorine-containing species (e.g., hydrogen chloride) in the flue gases. Felsvang, et. al., further teaches that this can be accomplished through the addition of a chlorine-containing agent to the combustion zone of the of the boiler, or through the injection of hydrochloric acid (HCl) vapor into the flue gases upstream of the SDA FGD. These techniques are claimed to improve the mercury removal performance of PAC when used in conjunction with an SDA FGD system.

[0010] SUMMARY OF THE INVENTION

Date Filed: Filed March 22, 2004

Title: DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GAS

[0011] It is an object of this invention to provide an inexpensive effective method for increasing the concentration of hydrogen chloride, or other halogen-containing compounds, on the surface of the carbonaceous sorbent as the sorbent is conveyed to the injection location.

[0012] It is another object of this invention to introduce through experimental testing that the use of bromine-containing compounds are significantly more effective than chlorine-containing compounds in enhancing the capture of elemental mercury by carbonaceous sorbents.

[0013] It is a further object of this invention to introduce a method of mercury removal that is applicable to virtually all coal-fired utility power plants, including those equipped with wet or SDA FGD systems, as well as those plants equipped only with particulate collectors.

#### [0014] BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Fig 1 is Relationship between coal mercury content and mercury speciation for U.S. coals.

[0016] Fig 2 is a view of the Dynamic Halogenation of Sorbents for the Removal of Mercury from Flue Gases.

[0017] Fig 3 is a Mercury Removal with Dynamic Halogenation Using Hydrogen Bromide chart.

[0018] Fig 4 is a Coal-Fired Utility Plant Equipped with a Particulate Collector.

[0019] Fig 5 is a Coal-Fired Utility Plant Equipped with an SDA FGD and Particulate Collector.

[0020] Fig 6 is a Coal-Fired Utility Plant Equipped with a Wet FGD and Particulate Collector.

#### [0021] DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Date Filed: Filed March 22, 2004

Title: DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GAS

[0022] The preferred embodiment of the current invention is illustrated in Figure 2. The system comprises conventional PAC injection system comprising a sorbent storage tank, a means for metering the sorbent into the sorbent transport air stream, a sorbent transport air blower supplying the air used to convey the sorbent to the injection locations in the flue gas duct(s), and a pick-up point where the sorbent is dispersed into the transport air stream. It should be recognized that this is only one embodiment of a pneumatic transport conveying system, and many other configurations could be used or developed by one of ordinary skill in the art without departing from the scope of the current invention. The key aspect of the current invention is that a halogen-containing gas is injected into the flowing transport air/sorbent stream at a point close to the point where the sorbent and transport air first mix. This is done to maximize the residence time available for the halogen-containing compound to be adsorbed onto the sorbent surface prior to the sorbent being injected into the flue gas duct. This process maximizes the benefit and utilization of the halogen-containing reagent by placing it exactly where it is needed to facilitate elemental mercury removal – on the surface of the sorbent. The sorbent particles with their loading of adsorbed halogen-containing reagent enter the flue gas duct with high reactivity for the removal of elemental mercury.

[0023] The present invention is advantageous to that of the prior art. The removal of elemental mercury from coal combustion gases generated by electric utility plants through the application of a conventional PAC injection process is very expensive. The current invention promises to significantly reduce the cost of mercury removal at coal-fired electric plants. First, the process provides the benefits, in terms of reactivity with elemental mercury, of using an expensive, treated PAC sorbent (e.g., iodine-impregnated PAC) while using a conventional, low-cost sorbent.

Date Filed: Filed March 22, 2004

Title: DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GAS

[0024] Relative to the addition of chlorine-containing compounds to the flue gases as taught by Felsvang, et. al. (U.S. Patent 5,435,980), the invention makes much more efficient use of the halogen-containing reagent by placing onto the carbon sorbent surface prior to injection into the flue gases. It has been found by the inventors, and by several other investigators, that the addition of hydrogen chloride gas to the flue gases upstream of the PAC injection system, as taught by Felsvang, et. al., does not significantly improve the elemental mercury removal performance of the PAC injection process. This is due to the fact that much of the injected hydrogen chloride reacts with other flue gas constituents (e.g., calcium compounds contained in the coal fly ash particles), thereby preventing it from enhancing the performance of the injected PAC. By making efficient use of the halogen-containing reagent, the invention permits much lower addition rates for the halogen-containing reagent relative to other methods for halogen addition. The invention also has the significant advantage over other means of adding halogen-containing compounds to the flue gases in that boiler and other power plant components are not subjected to the corrosive nature of the halogen compounds. This is especially true when compared to the addition of halogens to the boiler combustion chamber. High-temperature corrosion of boiler components by chlorides is a well-known and serious concern.

[0025] The invention was tested in a 5 million Btu/hr Small Boiler Simulator (SBS) Facility. The SBS was fired at approximately 4.3 million Btu/hr with a western U.S. subbituminous coal. The During the tests flue gases exiting the SBS boiler first passed through a spray dryer absorber (SDA) for removal of sulfur dioxide, and then through a fabric filter for removal of fly ash and spent sorbent from the SDA FGD system.

[0026] A stream of dynamically-halogenated PAC, prepared by the method of the current invention, was injected into the flue gas stream downstream of the SDA FGD, and upstream of

Date Filed: Filed March 22, 2004

Title: DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GAS

the fabric filter. Hydrogen bromide was used as the halogen-containing reagent, and a commercially-produced PAC was used as the carbonaceous sorbent. Figure 3 illustrates the removal of mercury across the SDA/FF system during operation of the Dynamic Halogenation process. It can be seen that upon injection of the dynamically-halogenated PAC, the vapor-phase mercury exiting the system dropped from its initial value of approximately 6 ug/dscm to well below 1 ug/dscm. Other significant observations included: 1) PAC injection, alone, at a similar injection rate provided no discernable mercury removal (due to the absence of acid gases in the flue gases), 2) the use of hydrogen bromide was significantly more effective than the use of hydrogen chloride, and 3) the rates of addition of both the hydrogen bromide and PAC are many times lower than the rates for other halogen addition processes and conventional PAC injection processes, respectively. These results identify the current invention offers a cost-effective method of removing elemental mercury from coal combustion flue gases.

[0027] In an alternative embodiment, as illustrated in Figure 2, wherein the halogen-containing reagent is either hydrogen bromide or bromine ( $\text{Br}_2$ ), a carbonaceous sorbent and halogen-containing reagent are brought together in the sorbent pneumatic transport line with sufficient residence time for the halogen-containing reagent to be adsorbed onto the carbonaceous sorbent particle before the sorbent is injected into the coal combustion flue gas stream.

[0028] In yet another embodiment the boiler fuel may be fired with, thus include, bituminous, subbituminous, and lignite coals and blends, thereof.

[0029] In yet another embodiment, the bromine-containing reagent could comprise hydrogen bromide gas ( $\text{HBr}$ ) or bromine ( $\text{Br}_2$ ).

Date Filed: Filed March 22, 2004

Title: DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GAS

[0030] In yet another embodiment, the halogen-containing gases may include any one or more of the following; hydrogen chloride, chlorine ( $\text{Cl}_2$ ), as well as compounds of fluorine and iodine.

[0031] In yet another embodiment, the carbonaceous sorbents may include, but are not limited to, powdered activated carbon (PAC), carbons and chars produced from coal and other organic materials, and unburned carbon produced by the combustion process itself.

[0032] In yet another embodiment, the electric utility plant configurations may include plants equipped with an SDA FGD and particulate collector (Figure 4), a particulate collector (Figure 5), and a wet FGD and particulate collector (Figure 6).

[0033] In yet another embodiment, the spent carbonaceous sorbent can be removed separately from the coal fly ash, if desired, by adding an additional particulate collector designed specifically to capture the injected quantity of carbonaceous sorbent.

[0034] There are other alternative embodiment as would be obvious to one of skill in the art based on the teaching of the present invention, and are intended to be included within the scope of the claims of this invention.

I claim:

1. A method of reducing the mercury concentration of a flue gas comprising;  

placing a halogen-containing reagent on a sorbent surface prior to injecting the sorbent surface into the flue gas.
2. A method of reducing the mercury concentration of a flue gas comprising the method as recited herein.

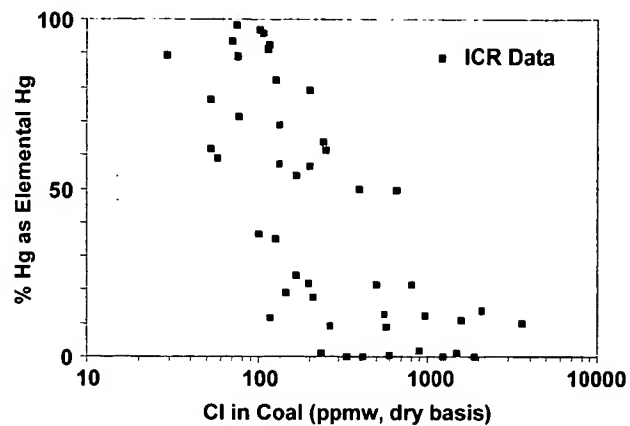


Fig. 1

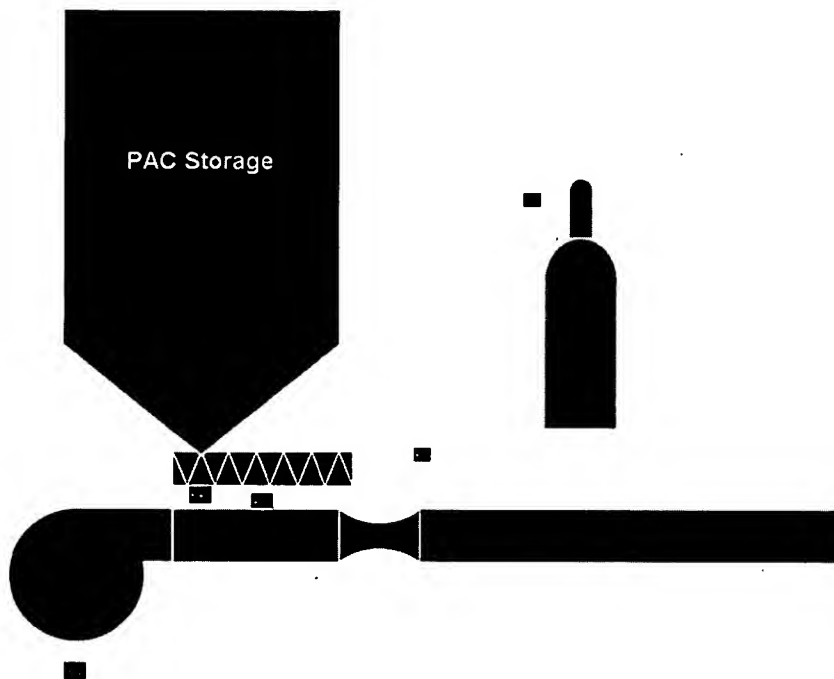


Fig 2

BEST AVAILABLE COPY

Date Filed: Filed March 22, 2004

Title: DYNAMIC HALOGENATION OF SORBENTS FOR THE REMOVAL OF MERCURY FROM FLUE GAS

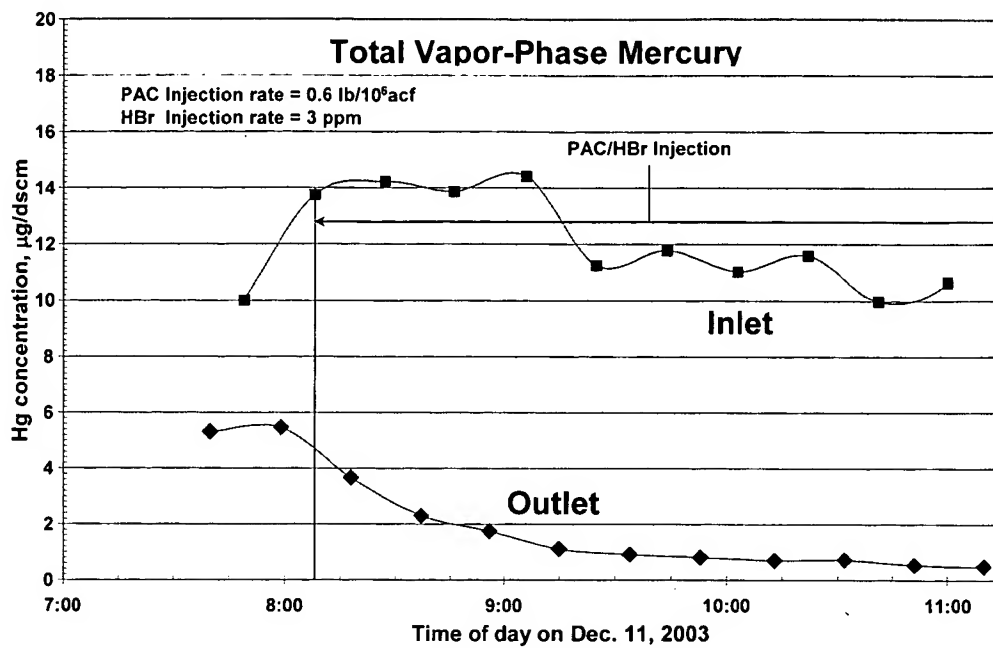


Fig 3

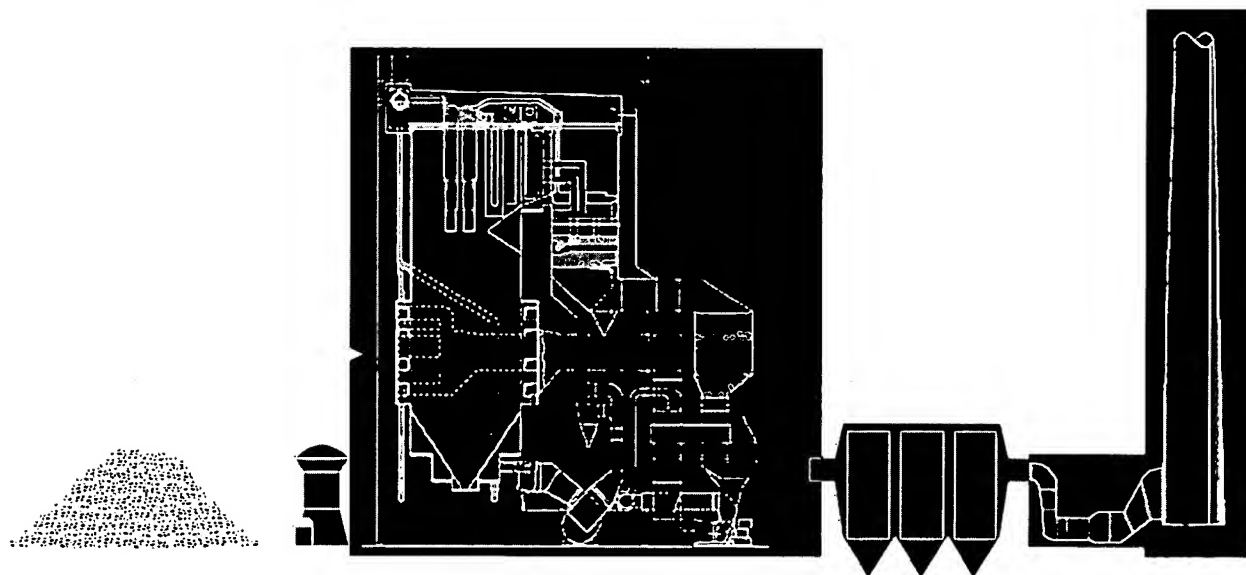


Fig 4.

BEST AVAILABLE COPY

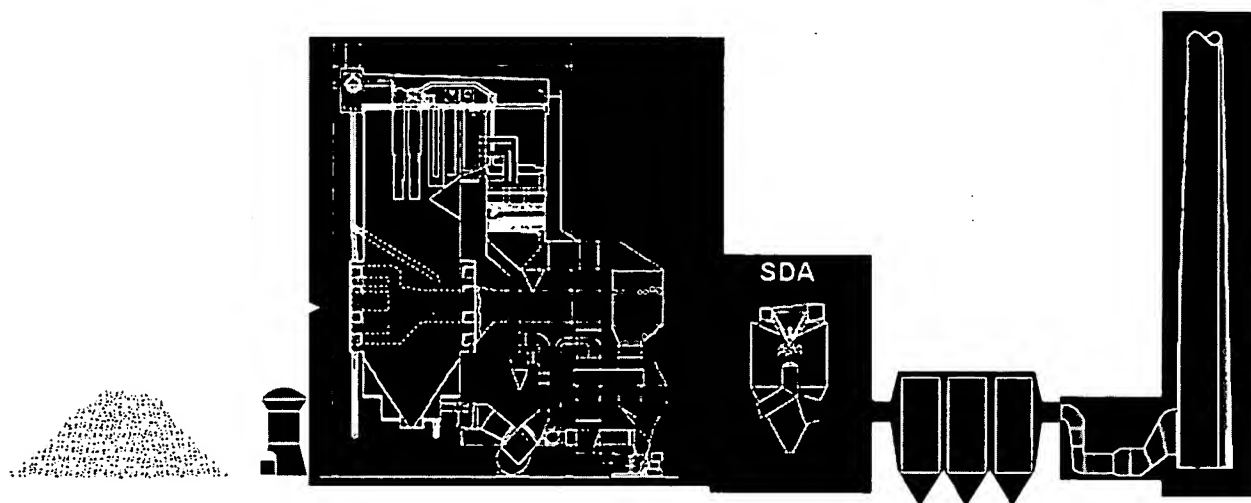


Fig. 5

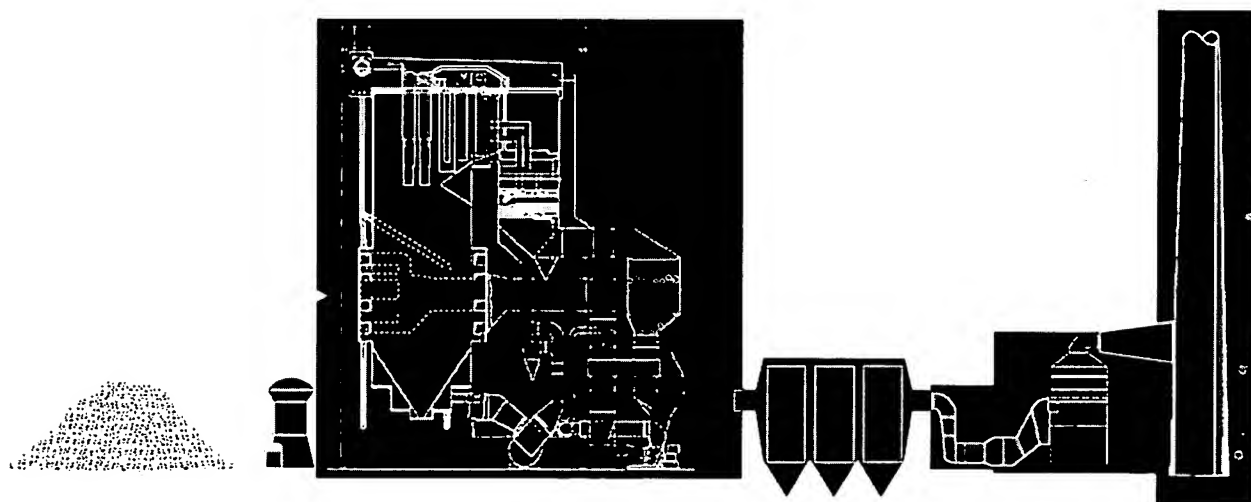


Fig 6

BEST AVAILABLE COPY